4. P. T. Petrov, V. M. Evdokimenko, and S. V. Markevich, Dokl. Akad. Nauk BSSR, 23, No. 7, 639 (1979).
5. V. B. Koziner and N. A. Fedorov, in: The Mechanism of the Action of Polyglucin [in Russian], Moscow (1974), p. 12.
6. J. M. Bailey and W. J. Whelan, J. Biol. Chem., 236, No. 4, 969 (161).

CARBOHYDRATES OF *Alium*.

VII. CHARACTERISTICS OF THE POLYSACCHARIDES OF THE SKIN OF *Alium cepa*

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UDC 547.917

The polysaccharides in the skin of the garden onion have been investigated. Their qualitative and quantitative compositions have been determined. The physicochemical characteristics of the pectin substances are given and the water-soluble polysaccharide is characterized.

Continuing investigations of the carbohydrates of plants of the family of Alliaceae [1], we have studied the carbohydrate composition of three samples of the skin of the garden onion *Allium cepa* (Samarkandskii krasnyi variety) obtained in the "serp i molot" ["Sickle and Hammer"] Preserving Combine (Samarkand). The first specimen was obtained after supplementary factory treatment with water at 95-97°C, and the second and third differed in their times of harvesting. From a single sample, after treatment with chloroform to eliminate extractive substances, the ethanol-soluble fraction (ES), the water-soluble polysaccharides (WSPSs) the pectin substances (PSs), and the hemicelluloses (HMCs) A and B were extracted successively with 96 and 80% ethanol. The results of the investigations are given in Table 1.

As can be seen from Table 1, the amounts of polysaccharides in this skin of the food onion were different, pectin substances predominating. The ethanol-solution fractions of samples I-III contained fructose, glucose, sucrose, and raffinose, which were identified by PC (system 1).

The WSPs-III formed a cream-colored powder readily soluble in water and insoluble in organic solvents. The molecular weight of the WSPs-III determined by gel chromatography on a column of Sephadex G-75 was 5700.

In the product of complete acid hydrolysis, fructose (main spot) and glucose (weak spot) were detected with the aid of PC (system 1). The IR spectrum was similar to the spectra of glucofructans of the mixed type [1].

Samples of the pectin substances and of the hemicelluloses A and B were subjected to complete acid hydrolysis. The hydrolysates were analyzed by PC (system 2) and GLC in the form of the corresponding aldononitrile acetates and polyol acetates [2].

The IR spectra of the pectin substances contained the absorption bands also characteristic for other pectins [3, 4].

Vibrations in the 1150 cm^{-1} region are probably connected with the maximum degree of esterification [3] and triplets of pyranose rings (815, 870, 910 cm^{-1}) show the presence of 1,4-bonds and the predominance of α-glycosidic bonds between the galacturonic acid and monosaccharide residues.

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Samarkand Cooperative Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 14-17, January-February, 1985. Original article submitted March 13, 1984.

 0009-3130/85/2101-0012$09.50

TABLE 1. Amounts of Carbohydrate Components and Their Monosaccharide Compositions

Product	Yield, % on the absolute dry raw material	Ratio of monosaccharides, molar						
		Fru	Gal	Glc	Rham	Xyl	Ara	GalUA
Sample I								
ES	2,0	+	—	+	—	—	—	—
WSPs	0,2	+	—	+	—	—	—	—
PSs	19,5	—	1,2	1,6	1,43	1,0	3,0	+
HMCs A	0,2	—	4,0	3,3	1.0	1,4	1,06	+
HMCs B	1,0	—	2,34	1,25	2,0	10,0	1,0	+
Sample II								
ES	13,0	+	—	+	—	—	—	—
WSPs	4,2	+	—	+	—	—	—	—
PSs	14,3	—	1,0	3,0	6,9	1,2	8,9	+
HMCs A	0,8	—	3,4	9,8	2,5	1	2,7	+
HMCs B	0,4	—	—	—	—	—	—	+
Sample III								
ES	12,4	+	—	+	—	—	—	—
WSPs	6,85	+	—	+	—	—	—	—
PSs	16,0	—	4,0	3,0	3,5	1,0	11,8	+
HMCs A	0,8	—	3,0	2,25	2,6	1,4	1,0	+
HMCs B	1,6	—	2,14	1,15	1,9	0,9	2,14	+

The molecular weights of the PSs were determined by the viscometric method [5] and by gel chromatography on a column of Sephadex G-100.

The high positive specific rotations of the PSs likewise permitted the assumption that the glycosidic bonds between the galacturonic acid residues in the pyranose form were in the α-configuration.

The physicochemical characterization of the PSs obtained by the titrimetric method [6] is given below (free carboxy groups — K_f; methoxylated carboxy groups — K_m; degree of methoxylation — λ; the amount or uronic anhydride was determined by a standard method [7]):

Sample	Mol. wt.	Sp. rotation, deg	Sp. viscosity (0.5%)	Uronic anhydride content, %	K_f	K_m	λ	OCH_3 %
I	45000	+200	0,25	53,7	4,05	2,0	33,4	1,47
II	40000	+174	0,21	46,6	3,98	1,85	31,7	1,3
III	39000	+175	0,23	45,0	3,97	1,83	31,6	1,28

In the products of the enzymatic hydrolysis with Fluka pectinase the same monosaccharide composition as in the case of complete acid hydrolysis was found for all the samples of pectin substances by PC (system 2).

EXPERIMENTAL

Paper chromatography was performed on Filtrak FN-16, 17 paper in the following systems: 1) water-saturated phenol; 2) 1-butan-ol—pyridine—water (6:4:3). The following reagents were used to indicate the spots: 1) 5% ethanolic solution of urea; 2) aniline hydrogen phthalate. IR spectra were taken on a UR-20 instrument in tablets with KBr. The specific rotations were determined on a Zeiss polarimeter in a tube 10 cm long with a volume of 10 ml. The GLC of the samples was performed on a Tsvet-101 instrument with a flame-ionization detector under the following conditions: steel column (0.200 × 0.3 cm), 5% Silicone XE-60 on Chromaton NAW (0.200-0.250 mesh) and a column temperature of 210°C with helium as the carrier gas at the rate of 40 ml/min. The aldonitrile acetates and polyol acetates were obtained as described by Lance and Jones [2].

Isolation of the Carbohydrate Components. The dry comminuted raw material (48.76 g) was treated with chloroform and extracted with 96 and 80% ethanol at the boiling point. The combined extracts (ES) were evaporated to a viscous syrup and after purification with carbon was subjected to PC (system 1).

The yield of the ES fraction was 0.97 g. The residue of the raw material was extracted with water, the extracts were evaporated and were purified with type OU-B charcoal, proteins

were eliminated by Sevag's method, and the products were precipitated with acetone. The yield of WSPSs was 0.1 g.

The raw material was then subjected to extraction with a 0.5% mixture of oxalic acid and ammonium oxalate at 70°C. After dialysis of the extracts, methanol precipitated 9.4 g of pectin. The raw material was then extracted with a 10% solution of NaOH at room temperature. After dialysis, a precipitate of hemicellulose A (0.1 g) deposited, and the mother solution was evaporated and precipitated with methanol to give the HMCs B (0.5 g).

Determination of Molecular Weights of the PSs and WSPSs by Gel Chromatography. Samples of 20 mg each of specimens I-III of the pectin substances from the skin of the garden onion and of dextrans (Ds) with molecular weights of 80,000, 40,000, and 10,000, in 2 ml of distilled water, were deposited successively on a column (54 × 1.7 cm) of Sephadex G-100, and samples of dextrans with molecular weights of 40,000 and 10,000 and of inulin and of raffinose on a column (45 × 1.2 cm) of Sephadex G-75. They were eluted with the same solution.

The column with the Sephadex G-100 was calibrated by the passage of D-80,000, V_e = 23.5 ml, of D-40,000, V_e = 32.1 ml, and of D-10,000, V_e = 45.5 ml. The eluates were collected at the rate of 3 ml/min and were analyzed by the phenol–sulfuric acid method. The molecular weights of the PS-I (V_e = 30 ml), the PS-II (V_e = 32 ml), and the PS-III (V_e = 32.5 ml) were determined from a graph of the dependence of the molecular weight on the elution volume as 45,000, 40,000, and 39,000, respectively. The column of Sephadex G-75 was calibrated by the passage of D-40,000 (V_e = 23.7 ml), D-20,000 (V_e = 30 ml), of insulin with mol. wt. 5600 (V_e 44.5 ml), and of raffinose with mol. wt. 504 (V_e = 63.5 ml). The molecular weight of the WSPS-III (V_e = 43 ml) was 5700.

The complete acid hydrolysis of samples of the PSs and of the HMCs A and B was carried out with 2 N H_2SO_4 at 100°C for 42 h. The hydrolysates were neutralized with $BaCO_3$ and after the elimination of the $BaSO_4$ by filtration, treatment with KU-4 (H^+), and evaporation to a syrup, PC showed the presence of glucose, galactose, rhamnose, arabinose, xylose, and galacturonic acid. The aldonitrile acetate and polyol acetate derivatives of these sugars were obtained for GLC.

A sample of the WSPS-III was hydrolyzed with 0.5 N H_2SO_4 at 100°C for 4 h. The hydrolysate was neutralized with $CaCO_3$, filtered, and evaporated to a syrup, and PC then showed the presence of fructose (main spot) and glucose (weak spot).

The enzymatic hydrolysis of samples of the PSs was performed with Fluka pectinase (Switzerland) in an acid medium, pH 4. Enzymatic hydrolysis lasted 48 h at 37°C. Then the enzyme was inactivated at 100°C for 5 min. The hydrolysis products were analyzed by PC (system 2), and the same monosaccharide composition was found as in the case of complete acid hydrolysis.

SUMMARY

The polysaccharides in the skin of the garden onion have been investigated. The qualitative and quantitiative compositions of the polysaccharides have been determined. They consist mainly of pectin substances and water-soluble polysaccharides.

The physicochemical characteristics of the pectin substances are given and the water-soluble polysaccharide-III is characterized.

LITERATURE CITED

1. M. A. Khodzhaeva and E. S. Kondratenko, Khim. Prir. Soedin., 105 (1984).
2. D. G. Lance and J. K. N. Jones, Can. J. Chem., 45, 1995 (1967).
3. E. P. Kukhta, V. Va. Chirva, M. R. Borovskii, M. A. Tomacheva, and I. V. Eremenko, Khim. Prir. Soedin., 275 (1982).
4. M. P. Filippov, Infrared Spectra of Pectin Substances [in Russian], Kishinev (1978), pp. 17, 21.
5. S. G. Kovalenko and S. D. Kurilenko, Usp. Khim. Zh., No. 31, 175 (1965).
6. G. V. Buzina, O. F. Ivanova, and L. B. Sosnovskii, Khlebopek i Konditersk. Prom-st, No. 4, 15 (1965).
7. M. N. Zaprometov, Biochemical Methods of Plant Analysis [in Russian], Moscow (1970), p. 296.